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KINETICS OF WATER VAPOUR SORPTION BY SELECTED INGREDIENTS OF MUESLI-TYPE MIXTURES

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Key words: muesli, water sorption, dried fruits, cereal flakes

Sorption properties of some ingredients of muesli such as flakes and dried and candied fruits were investigated in this work. Kinetics of water vapor sorption at water activity of 1.00, 0,755, 0.239 and 0.00 was continuously measured. Kinetics of water sorption was well described by the solution of the Second Fick's Law. However, the superficial values of equilibrium water content were obtained by kinetic measurements. The shape factor in the Fick's equation was dependent on water activity. It was shown that in the analysed products adsorption process goes faster than the desorption one. Hence desorption of water from fruits and adsorption by flakes seems to be a limiting factor for water transfer in mixtures consisting of cereals and fruits.

INTRODUCTION

Water is a significant factor affecting quality and shelf-life of food. Physical properties of a product, reactions influencing degradation of food ingredients and dietary values, they are all the function of water content and water activity [Bourne, 1990; Lewicki, 1999]. Water has also a key significance for a number of sensory attributes, specifically for the texture of food. In the case of crisp and brittle products, even small changes in water activity may cause significant changes in texture, which may lead to consumer's rejection of the product [Roudat *et al.*, 1998].

Products, whose water activity differs from that of the environment, tend to adsorb or give away (desorb) water during packing, storage (migration of water through the package), and preparation for consumption. Moreover, many of the recently popular "ready-to-eat" products are a very complicated system, in which water permanently migrates from one element to the other. This problem affects all products which consist of dry and wet ingredients like pizzas, dumplings, stuffed products, confectionery or ice-cream in wafer. It is difficult to achieve proper quality of such products as it is not always possible to separate all ingredients from each other using barrier substance for the water. A good example of such products are muesli-like mixtures. Cereals are distinctive for low water activity and for intensive sorption of water [Gondek & Lewicki, 2000], while dried fruits are products of medium water activity, which give away water when contacting a dry, hygroscopic product [Karathanos & Kostaropulos, 1995]. The adsorption and desorption processes usually lead to the loss of desired features in such mixtures and result in the consumer's rejection of the product. Hence, it may be useful to research the process of water sorption by ingredients of muesli-type mixtures in dynamic conditions both for projection and monitoring of the mass transfer processes in such mixtures.

MATERIALS AND METHODS

As a material of the investigation 4 types of cereals and dried and candied fruits available on the market were used in this experiment. The water content in cereals was measured according to PN-ISO:6540 by drying at 130-133°C for 4 h, while the fruits were vacuum dried at 70°C for 24 h. Water activity of both cereals and fruits were measured using Aqua Lab CX-2 (Decagon Devices Inc.) at 25±1.5°C, with the accuracy of ±0.003.

Changes in mass of the investigated materials at water activity of 1.00, 0,755, 0.239 and 0.00 were measured at 25 ±1.5°C within 48 h in the stand which allowed for continuous mass measurement. Water, saturated solutions of NaCl, I $MgCl_2$ and anhydrous $CaCl_2$ were used as hygrostatic salts. Changes in the sample mass were recorded every 1-10 min using the software POMIAR for DOS.

Mathematical analysis. Curves presenting relationship between water content and time at a given water activity were described with Table Curve 2D v3 [Jandel Scientific] by the following equations:

(a) for adsorption of water vapor:

$$\frac{u-u_r}{u_0-u_r} = A\exp(-K\tau) \qquad [1]$$

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(b) for desorption of water vapor:

$$\frac{u_r - u}{u_r - u_0} = A\exp(-K\tau) \qquad [2]$$

where: u - water content (g/100 g d.m.), K - coefficient (1/min), τ - time (min), A - shape factor, subscripts 0 and r are for initial and equilibrium, respectively, parameter K is related to water diffusion within the researched product by the equation:

$$K = \frac{D_e}{(\frac{L}{2})^2} \qquad [3]$$

where: D_e - effective diffusivity (m^2/s) and L - thickness of the material (m).

RESULTS AND DISCUSSION

The analysed products were taken directly from packages and put in environment of constant relative humilities. Products either absorbed or desorbed water (Figure 1). For example, in the environment with water activity of 0.329 cornflakes and wheat bran adsorbed water, while other products were desorbing water. The most intense adsorption took place at the relative humidity equal to 1(Figure 2). Under such conditions, the highest equilibrium water content calculated from equation [2] was observed for raisins: 107.4 g of water/100 g d.m., while the lowest was measured for mango fruit: 52.2 g of water/100 g d.m. Also over the twofold difference in the amount of adsorbed water was observed for cornflakes and wheat bran flakes. In both groups, the products differ significantly by the ability to adsorb water.

None of the analysed products reached the equilibrium within the timeframe set for the tests (Figure 2). Products differed both in initial water activity and the content of water, which means that the driving force of the sorption process was also different. Depending on the water activity of the environment, sorption proceeded with different intensity. Regardless of that, in each case the largest changes in water activity were observed during the initial 10 h of the process. Water content was calculated after that time, and the difference between initial content of water and its value after 10 h of sorption [d U] was plotted as a function of the driving force that is the difference between water activity of the product taken directly from the package and water activity of the environment (d a_w) (Figures 3 and 4).

It was observed that in each case changes of water content per unit change of water activity were larger for adsorption than for desorption. Hence, the adsorption process is considered to be faster than the desorption one, which means that a product adsorbs water much easier than gives it away. Similar conclusions were reached while investigating the process of mass exchange in muesli mixtures [Gondek, 2003] or analysing water sorption isotherms for many food products [Lewicki & Pomarańska-Łazuka, 2003].

Cornflakes and wheat bran flakes were especially reluctant to give away water among the group of the investigated products. The most significant difference between the rate of

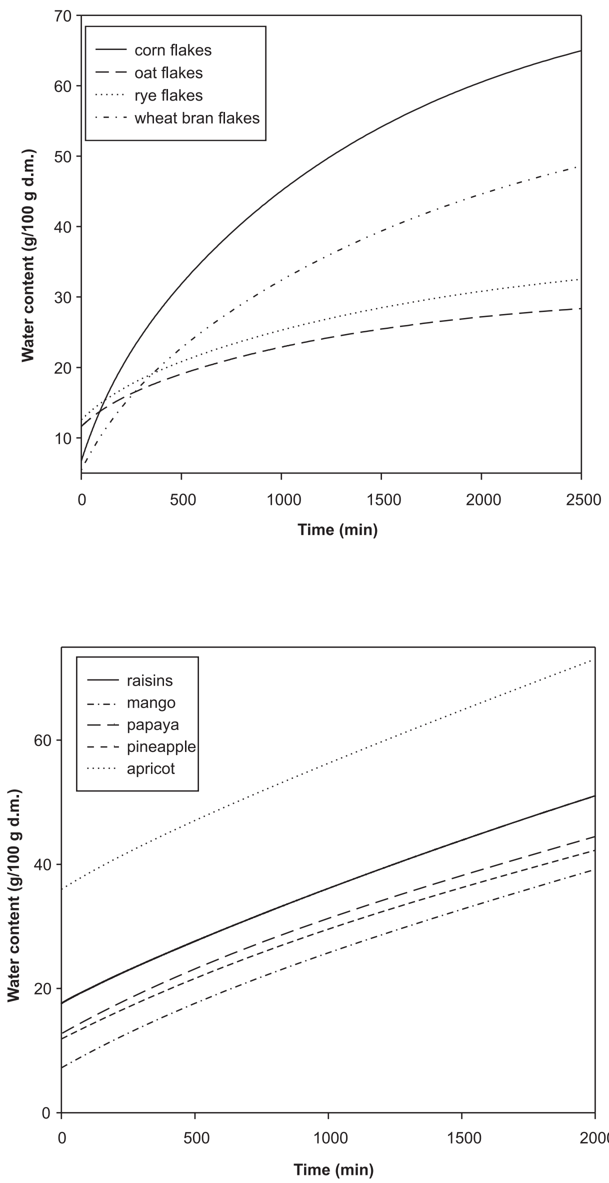

FIGURE 2. Relationship between water content of the investigated products and time of the sorption process at water activity 1.

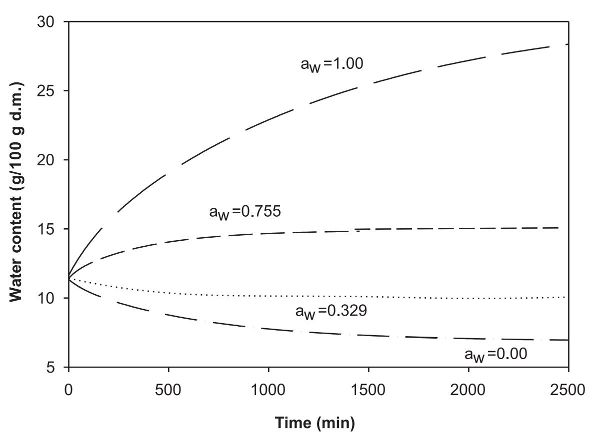

FIGURE 1. Relationship between water content in rye flakes and time of sorption different water activity of environment.

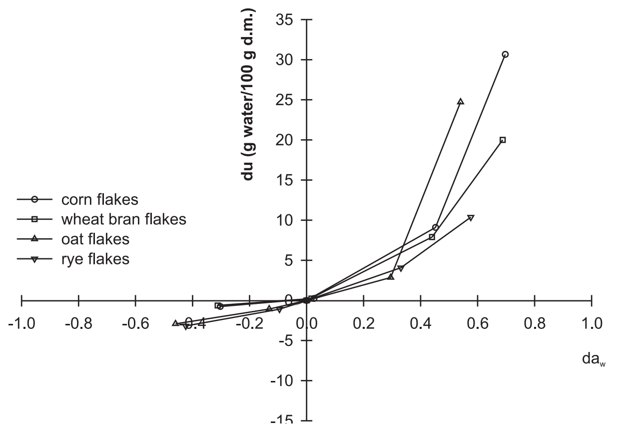

FIGURE 3. Relationship between changes in water content in cereal flakes and sorption driving force.

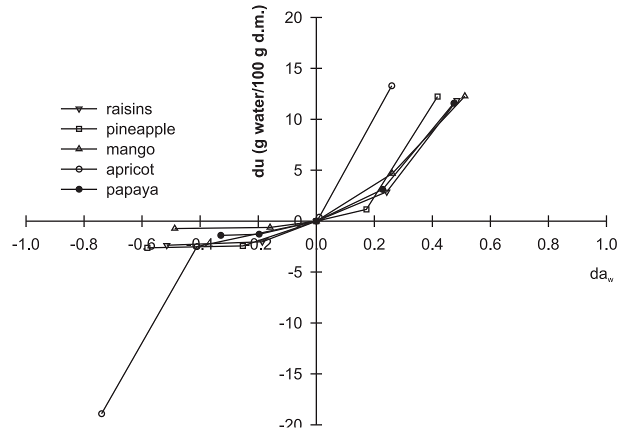

FIGURE 4. Relationship between changes in water content in dried fruits and sorption driving force.

TABLE 1. Coefficients of equation [2] and [3].

a_w	Corn flakes	Wheat bran flakes	Oat flakes	Rye flakes	Pineapple	Mango	Apricot	Papaya	Raisins
0.00	Desorption u_r=4.59 K=1.28·10^{-3} A=0.7868 r^2=0.9926	Desorption u_r=4.29 K=3.62·10^{-4} A=0.7443 r^2=0.9753	Desorption u_r=6.86 K=6.12·10^{-4} A=0.8939 r^2=0.9990	Desorption u_r=7.52 K=8.05·10^{-4} A=0.8662 r^2=0.9967	Desorption u_r=8.70 K=1.81·10^{-3} A=0.8951 r^2=0.9936	Desorption u_r=6.17 K=1.81·10^{-3} A=0.8281 r^2=0.9947	Desorption u_r=14.43 K=3.8·10^{-3} A=0.9749 r^2=0.9977	Desorption u_r=8.99 K=8.5·10^{-4} A=0.8683 r^2=0.9997	Desorption u_r=13.95 K=1.77·10^{-3} A=0.9461 r^2=0.9929
0.329	Adsorption u_r=6.15 K=2.13·10^{-4} A=0.9183 r^2=0.9972	Adsorption u_r=5.95 K=1.74·10^{-4} A=0.8358 r^2=0.9931	Desorption u_r=10.04 K=1.03·10^{-4} A=0.8261 r^2=0.9919	Desorption u_r=10.42 K=9.04·10^{-4} A=0.8052 r^2=0.9834	Desorption u_r=8.47 K=1.3·10^{-3} A=0.8962 r^2=0.9928	Desorption u_r=6.1759 K=1.45·10^{-3} A=0.8783 r^2=0.9935	Desorption u_r=29.45 K=7.57·10^{-4} A=0.9725 r^2=0.9958	Desorption u_r=9.37 K=1.01·10^{-3} A=0.910 r^2=0.9998	Desorption u_r=13.51 K=1.14·10^{-3} A=0.9693 r^2=0.9899
0.755	Adsorption u_r=18.74 K=7.32·10^{-4} A=0.9465 r^2=0.9979	Adsorption u_r=18.75 K=5.56·10^{-4} A=0.9286 r^2=0.9985	Adsorption u_r=14.94 K=1.02·10^{-3} A=0.8834 r^2=0.9997	Adsorption u_r=17.08 K=9.14·10^{-4} A=0.2761 r^2=0.9999	Adsorption u_r=15.93 K=1.68·10^{-3} A=0.9601 r^2=0.9988	Adsorption u_r=24.26 K=4.94·10^{-4} A=0.9808 r^2=0.9991	Adsorption u_r=37.13 K=1.84·10^{-3} A=0.9720 r^2=0.9958	Adsorption u_r=21.64 K=6.3·10^{-4} A=0.9885 r^2=0.9888	Adsorption u_r=29.50 K=4.37·10^{-4} A=0.989 r^2=0.9976
1.00	Adsorption u_r=77.38 K=2.57·10^{-4} A=0.8579 r^2=0.9970	Adsorption u_r=60.58 K=2.30·10^{-4} A=0.8984 r^2=0.9998	Adsorption u_r=31.59 K=2.89·10^{-4} A=0.8836 r^2=0.9993	Adsorption u_r=37.61 K=2.38·10^{-4} A=0.8564 r^2=0.9985	Adsorption u_r=62.20 K=4.68·10^{-4} A=0.9949 r^2=0.9997	Adsorption u_r=52.34 K=5.22·10^{-4} A=0.9933 r^2=0.9996	Adsorption u_r=81.45 K=5.73·10^{-4} A=0.9973 r^2=0.9998	Adsorption u_r=70.18 K=3.6·10^{-4} A=0.9957 r^2=0.9999	Adsorption u_r=107.39 K=2.33·10^{-4} A=0.9969 r^2=0.9954

adsorption and desorption was observed for cornflakes, while the smallest - for rye flakes. For fruits, the biggest difference between adsorption and desorption was observed for mango. Curves plotted for pineapple, mango, papaya and raisins are almost coincident during adsorption. Apricot tends to behave differently from other fruits, which may be explained by the lower content of sugar as well as the presence of skin covering the fruit which may affect the process of sorption (products were not reaching equilibrium).

Based on the results obtained, it may be supposed that in mixtures consisting of cereals and dried fruits, in which particular ingredients adsorb and desorb water respectively, the rate of the mass exchange will be mainly dependant on products which give water away. It was proved that in the analysed products desorption processes were slower than the adsorption ones, so the main resistance to mass transfer must come from products desorbing water. Hence, in muesli-type mixtures, it is fruits' ability to desorb water that is an important factor constraining water diffusion among the mixture ingredients.

The equilibrium water content after the infinite period of storage, shape coefficient A and coefficient K were calculated from equations [1] and [2] are shown in Table 1.

The equilibrium moisture obtained by extrapolation of kinetic measurements differs from the equilibrium moisture as recorded under static conditions [Gondek, 2003]. The results show that kinetic measurements do not allow to determine parameters for equilibrium state. Thus the extrapolation of water content obtained from equation [1] and [2] can only describe a pseudo-equilibrium state, which differs from the values derived from sorption isotherms.

Table 1 presents how the water activity of environment affects the shape coefficient A. The results obtained tend to confirm that the majority of the investigated products change their shape due to sorption or desorption of water. No such effect was observed in rye or oat bran while it was very distinct in fruits. In the case of papaya, raisins and mango, the coefficient A grows when the material adsorbs water and decreases when desorption appears. Apricot fruit starts to change its shape distinctly (it swells) only when the water activity of environment is at 1 since at that water activity it starts to adsorb water. In the environment with the water activity below or equal the water activity of the product taken from the package (when the product is subject to desorption), no changes to the shape of apricot fruit were observed.

No relationship was observed between water activity and coefficient K. Coefficient K is related to diffusion coefficient which tends to decrease with decreasing water content, in the investigated products. However the characteristic dimension L is present in the coefficient K in second power (eq. [3]), thus any changes in L make that the information that it carries about the rate of vapor sorption becomes ambiguous.

CONCLUSIONS

1. Curves for kinetics of water vapor sorption by cereals as well as dried and candied fruits may be described with Fick's equation for transient diffusion, however they do not represent the actual equilibrium state when obtained by extrapolation of water content.

2. The shape coefficient in Fick's equation for the investigated products depends on water activity, and it may express swelling and changes in shape and texture of the material.

3. In the analysed products, the adsorption process is faster than the desorption one, so it seems to be a limiting factor for water transfer in mixtures consisting of cereals and fruits.

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KINETYKA SORPCJI PARY WODNEJ PRZEZ WYBRANE SKŁADNIKI MIESZANEK TYPU MESLI

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Celem pracy była analiza właściwości sorpcyjnych wybranych składników mieszanek typu muesli: płatków zbożowych i owoców. Kinetykę sorpcji pary wodnej w aktywnościach wody: 1,00, 0,755, 0,239 i 0,00 wyznaczono na stanowisku zapewniającym ciągły pomiar masy próbki. Uzyskane krzywe kinetyki sorpcji pary wodnej opisano równaniami dyfuzji nieustalonej Ficka przy użyciu programu Table Curve 2D v3. Obliczono równowagową zawartość wody w produkcie, u_r, współczynnik kształtu A, oraz parametr K, który informuje o współczynniku dyfuzji wody w badanym materiale. Wykazano, że uzyskane drogą ekstrapolacji wilgotności nie reprezentują rzeczywistego stanu równowagi, a współczynnik kształtu badanych produktów, zależy od aktywności wody, co może być wyrazem pęcznienia i zmian kształtu i faktury powierzchni adsorbenta. Wykazano ponadto, że proces adsorpcji przebiega w analizowanych produktach szybciej niż desorpcji, jest więc on procesem limitującym ruch wody w mieszankach płatków z owocami.